Journal of Nuclear Materials 443 (2013) 17–19

Contents lists available at SciVerse ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

A thermodynamic model of thermal end elastic properties of curium

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ARTICLE INFO

Article history:
Received 22 May 2013
Accepted 21 June 2013
Available online 2 July 2013

ABSTRACT

A self-consistent thermodynamic model of curium is developed. In the framework of this model the temperature dependencies of heat capacity, coefficient of thermal expansion, bulk modulus and Debye temperature of Cm are calculated. It is shown that the phonon anharmonicity of Cm is weaker than in the case of Np and δ-Pu, but stronger than in lanthanides.

1. Introduction

The investigations of thermal and elastic properties of curium are quite scarce: the experimental data on the heat capacity is absent and the data on the density [1], coefficient of thermal expansion [1] and bulk modulus [2] are limited by the values near the room temperature. In the paper [3], proceeding from the comparison of the thermophysical and thermochemical properties of the lanthanide and actinide series, it has been pointed to the possible identity of the entropies and heat capacities of curium and gadolinium. However, according to the results of ab initio calculations [4,5] the electronic structures of these two metals are different and thus the influence of the electronic subsystem on the heat capacity of curium and gadolinium cannot be the same. Moreover, one has to expect considerable difference in the values of lattice anharmonicity parameters and of related thermal and elastic properties of these metals.

In the present study a simulation of temperature dependences of the thermal and elastic properties of Cm is carried out in terms of the self-consistent thermodynamic model [6–8], which along with the lattice properties accounts for the effect of electronic subsystem.

2. Model description

Following [6–8] we consider the connection of Debye temperature θ with molar volume V and bulk modulus B in the form

$$\theta = \frac{\hbar}{k_B}\left(6\pi^2 N_A^2\right)^{1/3}\sqrt{\frac{3}{\mu}}\Xi^{1/2}B^{1/2}V^{1/6}, \tag{1}$$

where $\hbar$, N_A are Plank and Avogadro constants, respectively; μ is the molar mass and $\Xi(\sigma)$ is a function of the Poisson coefficient σ. We define the thermodynamic potential (TDP) in the additive form $\Phi = \Phi_0 + \Phi_{ph}$, where $\Phi_0 = \Phi_0(P)$ is the "constant" part of TDP, which is temperature independent, but is a function of pressure; $\Phi_{ph} = \Phi_{ph}(\theta(P), T)$ is the molar lattice (phonon) part of TDP responsible for the contribution of acoustic vibrations of a solid:

$$\Phi_{ph} = 3R\left(\frac{3}{8}\theta + T\phi(z)\right), \tag{2}$$

where $z = \theta/T$ is the inverse reduced temperature and $\phi(z) = \ln(1 - e^{-z}) - D(z)/3$ ($D(z)$ is the standard tabulated Debye function). From Eqs (1) and (2) it follows that the characteristic Debye temperature enters the definition of the phonon part of TDP $\Phi_{ph} = \Phi_{ph}(\theta(P), T)$ and at the same time θ is a function of temperature. Since all the calculated thermal and elastic properties are defined from the phonon TDP $\Phi_{ph} = \Phi_{ph}(\theta, T)$, the change of the simulated values of Debye temperature leads the change of these properties. The simulation of the properties, in turn, leads to renormalization of the array of Debye temperature values. This allows to construct an iterative procedure for the self-consistent calculations of temperature dependencies of θ, thermal and elastic properties and account for the effects of phonon anharmonicity.

The developed procedure has to be supplemented by self-consistent accounting of the effect of electronic subsystem. This is done by adding the corresponding expression for electronic contribution to the lattice part of heat capacity. Thus for the contributions to heat capacity we have

$$C_{ph}(T) = -T\frac{\partial^2\Phi}{\partial T^2} = 3R\left\{C_{VR}(z)\left[1 - \frac{1}{z}\left(\frac{\partial\theta}{\partial T}\right)_P\right]^2 - T\left[\frac{3}{8} + \frac{D(z)}{z}\right]\left(\frac{\partial^2\theta}{\partial T^2}\right)_P\right\},$$

$$C_{el}(T) = \frac{\pi^2 k_B^2 N_A}{3}\sum_{l=0}^{3} g^{(l)}(\mu)T, \tag{3}$$

where $C_{VR}(z)$ is the standard Debye heat capacity, normalized to $3R$, $g^{(l)}(\mu)$ is the densities of states at the Fermi energy of the electrons of the lth band and k_B is Boltzmann constant.

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http://dx.doi.org/10.1016/j.jnucmat.2013.06.036

From the expression (3) one can see that in the absence of temperature dependence of the Debye temperature, the phonon heat capacity coincides with the Debye heat capacity $C_{VR}(z)$, i.e. with the heat capacity calculated within harmonic approximation. In our model we obtain an additional contribution to the heat capacity associated with the phonon anharmonicity.

In our approach we also calculate the molar volume defined by the expression $V(T) = \left(\frac{\partial \Phi}{\partial P}\right)_T = V_0 - \frac{3R\theta\gamma_\theta}{B}\left(\frac{3}{8} + \frac{D(z)}{z}\right)$, where V_0 is the volume at $T = 0$ K and the second term is the lattice contribution. The negative sign in this expression is due to the fact that the generalized Gruneisen parameter for the Debye temperature $\gamma_\theta = \frac{V}{\theta}\left(\frac{\partial \theta}{\partial V}\right)_{TP}$ is intrinsically negative, since the Debye temperature is reduced with increase in volume (and temperature).

Then for the phonon part of volumetric thermal expansion coefficient (VCTE) we obtain the following formula

$$O(T) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{3R\theta\gamma_\theta}{VB}\left\{C_{VR}(z)\left[1 - \frac{T}{\theta}\left(\frac{\partial \theta}{\partial T}\right)_P\right]\frac{1}{\theta} + \left[\frac{3}{8} + \frac{D(z)}{z}\right]\cdot\left[\frac{1}{\theta}\left(\frac{\partial \theta}{\partial T}\right)_P + \frac{1}{\gamma_\theta}\left(\frac{\partial \gamma_\theta}{\partial T}\right)_P - \frac{1}{B}\left(\frac{\partial B}{\partial T}\right)_P\right]\right\}. \quad (4)$$

And finally for the bulk modulus one can derive

$$B(T) = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T = B_0 + \frac{3R}{V}\left\{\frac{3}{8}\gamma_\theta^* \theta - T\left[\gamma_\theta^* \cdot C_{VR}(\theta/T) - \gamma_\theta^* \cdot D(\theta/T)\right]\right\}. \quad (5)$$

The γ_f and γ_f^* parameters, appearing in the equations above, are generalized Gruneisen parameters, which for a thermodynamic quantity $f = f(T, V)$ at constant temperature and pressure are defined as

$$\gamma_f = \frac{V}{f}\left(\frac{\partial f}{\partial V}\right)_{TP}; \quad \gamma_f^* = \frac{V^2}{f}\left(\frac{\partial^2 f}{\partial V^2}\right)_{TP}. \quad (6)$$

The starting (at $T = 0$ K) values of the Gruneisen parameters for bulk modulus γ_{B0}, γ_{B0}^* and for Poisson coefficient γ_σ, γ_σ^* as well as the Poisson coefficient σ itself represent the parameters of the model.

3. The results and discussion

Evaluating the input parameters of our model for Cm as the initial data we use the data on the lattice heat capacity of gadolinium (isostructural 4f analog of curium), which has been obtained in the self-consistent thermodynamic model [8]. In addition, we account for the available experimental data on the thermal expansion and bulk modulus of Cm. The coefficient of electronic heat capacity $\gamma = 3.3$ mJ/(mol K^2) has been evaluated by taking the data [4] on the electronic structure of Cm, according to which the total density of states at the Fermi energy of Cm equals 1.4 1/(eV atom). It should be noted that the electronic densities of states of Cm are rather flat near the Fermi energy [4], so the coefficient of electronic heat capacity of Cm can be assumed to be almost temperature-independent up to the highest temperature considered in the present study. Eventually, we have obtained the following values for the thermodynamic parameters of Cm: $\gamma_{B0} = -0.12$, $\gamma_{B0}^* = 1.14$, $\sigma = 0.270$, $\gamma_\sigma = 1.20$, $\gamma_\sigma^* = 1.03$.

The results of calculations of the temperature dependence of Cm molar heat capacity are presented in Fig. 1. It should be noted that in the present study calculations were performed for the paramagnetic phase of Cm, while the spin-fluctuation anomalies of the heat capacity associated with the antiferromagnetic transition ($T_N \sim 52$ K [9]) has not been considered. Since the experimental data on the heat capacity of Cm is absent, the heat capacity of paramagnetic phase of gadolinium [10] is shown in Fig. 1 for comparison. One can see that although the calculated total heat capacity of Cm is similar to the experimental heat capacity of Gd, there are certain differences between them. In the inset to Fig. 1 the "one-electron" heat capacity of Cm is compared with the contribution of phonon anharmonicity, which was obtained by subtracting the phonon contribution at constant volume C_v from the phonon contribution at constant pressure C_p; the latter was calculated with self-consistently defined Debye temperature. One can see that in the entire temperature range the electronic subsystem has greater effect on heat capacity of Cm as compared to phonon anharmonicity. However, the low-temperature coefficient of electronic heat capacity of Cm is sufficiently smaller than in case of americium [11], which precedes curium in the periodic table.

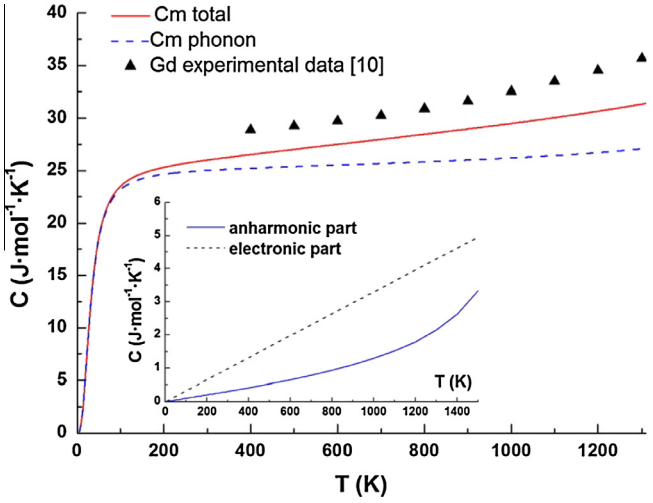

Fig. 1. Temperature dependence of the molar heat capacity of curium; inset: comparison of different contributions to the heat capacity of Cm.

In Fig. 2 we present the results of our calculations of the linear coefficient of thermal expansion (LCTE) of Cm in comparison with the experimental data [1], which are limited to a single value averaged over the temperature range 90–300 K; therefore these data are shown by horizontal lines in Fig. 2. Because the crystal structure of Cm is dhcp [1], LCTE of Cm is different for crystallographic

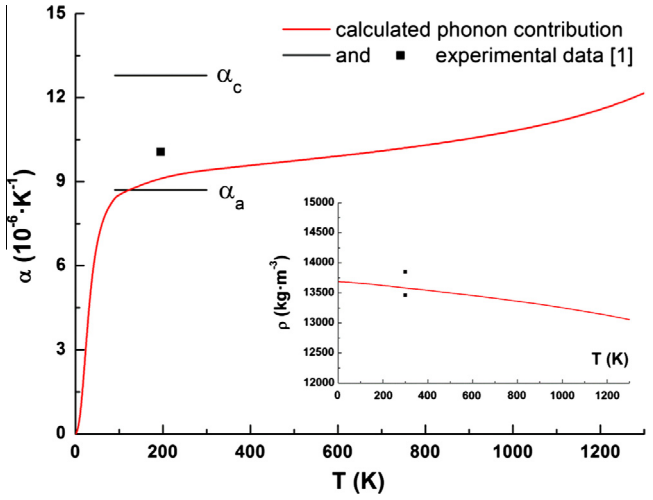

Fig. 2. Temperature dependence of the linear coefficient of thermal expansion; inset: temperature dependence of the mass density of Cm.

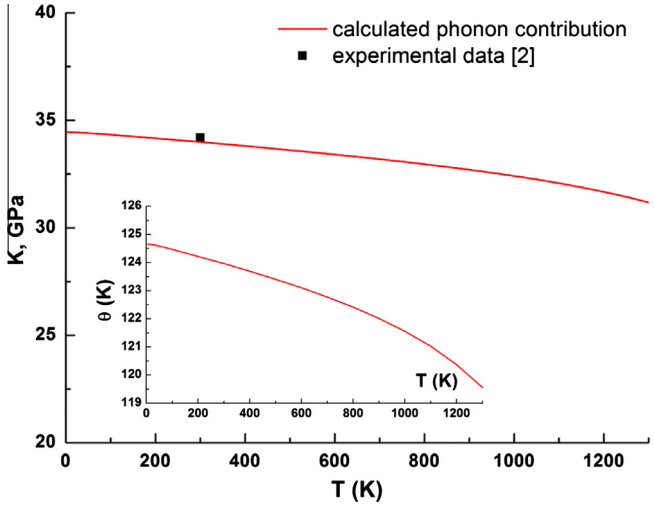

Fig. 3. Temperature dependence of the bulk modulus of curium; inset: the Debye temperature of Cm.

axes *a* and *c*, and the black square in Fig. 2 corresponds to the value averaged over axes at averaged temperature 195 K (because our calculations can be performed only for the averaged along the *a* and *c* axes values). In the inset to Fig. 1 we show the results of calculations of curium mass density in comparison with the experimental data [1], which again are limited to values at $T = 300$ K for two different samples.

Obtained in the present study temperature dependence of the bulk modulus of Cm is presented in Fig. 3, while the inset to Fig. 3 shows the calculated Debye temperature of Cm. One can see that Debye temperature of Cm is essentially lower than Debye temperature of Gd, which according to [8] is of about 170 K. The bulk modulus of Cm rather weakly depends on temperature as compared with e.g. Np [6] and δ-Pu [7], which indicates that Cm can be characterized by relatively weak phonon anharmonicity. This fact is confirmed by the calculated contribution of phonon anharmonicity to the heat capacity of Cm and by the values of Gruneisen parameter $\Gamma = -\frac{\partial \ln \theta}{\partial \ln V}$ of Cm, which in the temperature range up to 1300 K does not exceed $\Gamma = 0.86$ (while for Np even at the room temperature $\Gamma = 2.70$).

In Table 1 we compare the parameters characterizing the degree of phonon anharmonicity of curium (the present study), neptunium [6], gadolinium and lutetium [8] – the latter two being representatives of the lanthanide (4f metals) series. It follows from Table 1 that phonon anharmonicity of Cm although being weaker than of Np, manifests in Cm stronger than in Gd and is almost

Table 1
Phonon anharmonicity parameters for some representatives of actinide and lanthanide series.

	Cm	Np	Gd	Lu
σ	0.270	0.330	0.260	0.219
$\Gamma(T = 300\ \mathrm{K})$	0.71	2.70	0.44	0.83
$\alpha_{ph}(T = 300\ \mathrm{K})$, $10^{-6}\ \mathrm{K}^{-1}$	9.34	20.50	5.0	7.46
$\Gamma \cdot \alpha_{ph}(T = 300\ \mathrm{K})$, $10^{-6}\ \mathrm{K}^{-1}$	6.63	55.35	2.20	6.19

the same as in Lu. Despite Lu has larger value of the Gruneisen parameter $\Gamma(T = 300\ \mathrm{K}) = 0.83$ than $\Gamma(T = 300\ \mathrm{K}) = 0.71$ in the case of Cm, at the same time Lu exhibits lower thermal expansion coefficient $\alpha_{ph}(T = 300\ \mathrm{K}) = 7.46 \times 10^{-6}\ \mathrm{K}^{-1}$. Therefore the product $\Gamma \cdot \alpha_{ph}(T = 300\ \mathrm{K})$, which is the generalized measure of phonon anharmonicity [12], is larger in the case of Cm (and further more in the case of Np).

Thus the thermodynamic model formulated in the present study points to rather essential difference between the lattice properties of Cm and lanthanide metals as well as other actinides. Although the developed model is based upon some experimental data on thermal and elastic properties of Cm, to verify these data rather big amount of experimental investigations of Cm is yet to be done, at least of such important properties as heat capacity, thermal expansion coefficient and bulk modulus.

Acknowledgement

This study was supported by The Ministry of education and science of Russian Federation, Project 14.A18.21.0737.

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